Supporting Information

Substitution Position Regulating the Excitation-Dependent Fluorescence-Phosphorescence Emission of Formylphenylboronic Acids for Single-Component White Light and Anticounterfeiting

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Materials and instrumentation. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde was bought from Energy Chemical. 4-Formylphenylboronic acid was obtained from Adamas. 2-Formylphenylboronic acid and 3-formylphenylboronic acid were both bought from Innochem. High performance liquid chromatography (HPLC) analysis was measured on a Shimadzu LC-20AT system. Elemental analysis was carried out on PerkinElmer 2400II or Elementar Unicube elemental analyser. Absorption spectra in 2-methyltetrahydrofuran solution were measured on a Shimadzu UV-2600 spectrophotometer. Solid-state absorption was conducted on a Shimadzu UV-3600 Plus spectrophotometer using diffuse reflectance mode. Photoluminescence measurements were all conducted on an Edinburgh Instruments FLS1000. Powder X-ray diffraction was done on a Bruker D8 Focus diffractometer.

Single-crystal X-ray diffraction was collected on a Bruker APEX-II CCD diffractometer. The crystal structures were solved by the direct method and then refined by a full-matrix least squares technique on F^2 using SHELXL programs.[1,2] CCDC 2267832 (2-FPBA) and 2267833 (3-FPBA) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational detail. For the solid-state calculation, the geometries were

directly extracted from the crystal structure without further optimization. The electronic transition energies and the SOC constants were calculated on Orca 5 at CAM-B3LYP/ZORA-def2-TZVP level.[3] Hirshfeld surface analysis was conducted on CrystalExplorer.[4]

Purification detail. 2-FPBA, 3-FPBA, and 4-FPBA commercial samples were further purified by recrystallizing from distilled water. 4-TMBBA was purified by column chromatography (petroleum ether as the eluent). The purity were checked by elemental analysis or HPLC. The results list in Table S1 and Figure S1.

Table S1. Elemental analyses of three FPBA position isomers.

	Calcd (%)	Found (%)
2-FPBA	C, 56.07; H, 4.71	C, 56.00; H, 4.55
3-FPBA	C, 56.07; H, 4.71	C, 55.80; H, 4.63
4-FPBA	C, 56.07; H, 4.71	C, 56.00; H, 4.59

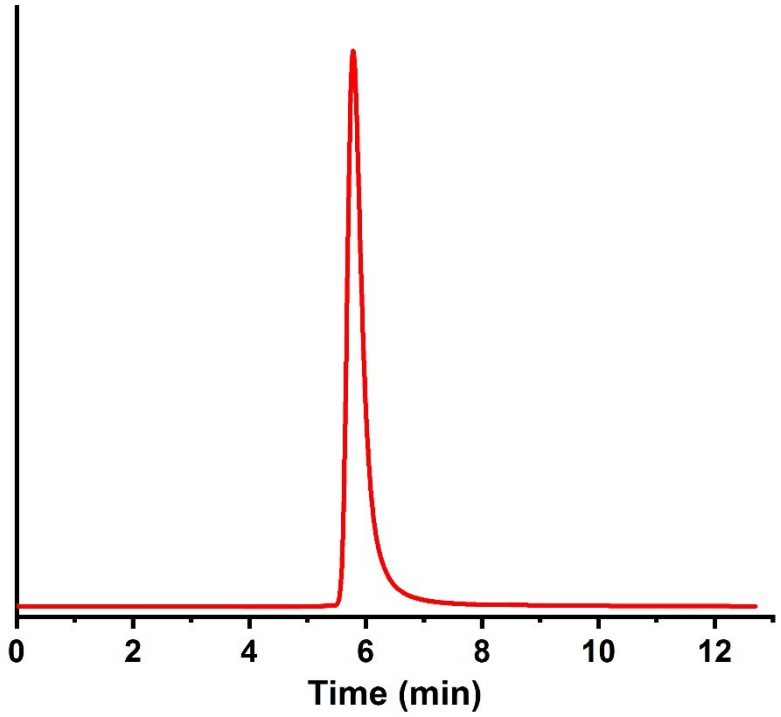

Figure S1. HPLC curves of 4-TMBBA in pure methanol by monitoring at 254 nm.

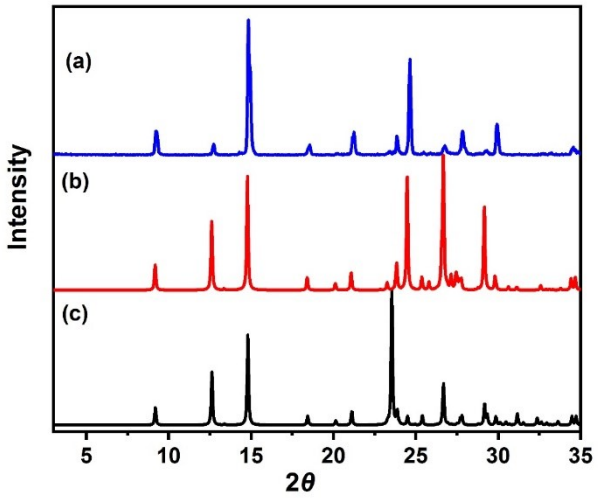

Figure S2. (a) X-ray diffraction (XRD) pattern of 2-FPBA powder. (b) Simulated XRD pattern from the single-crystal structure reported here (CCDC-2267832). (c) Simulated XRD pattern from the previously reported single-crystal structure (CCDC-1302472).

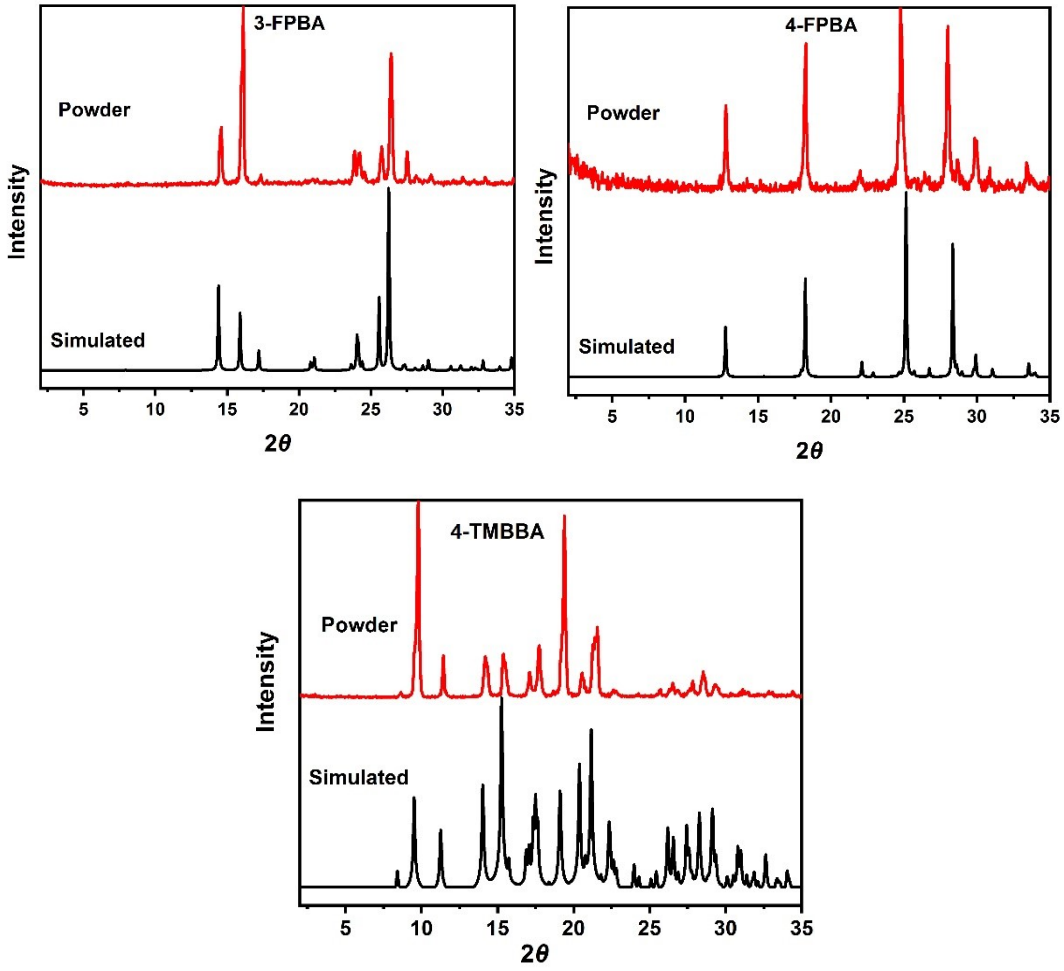

Figure S3. XRD patterns of 3-FPBA, 4-FPBA, and 4-TMBBA.

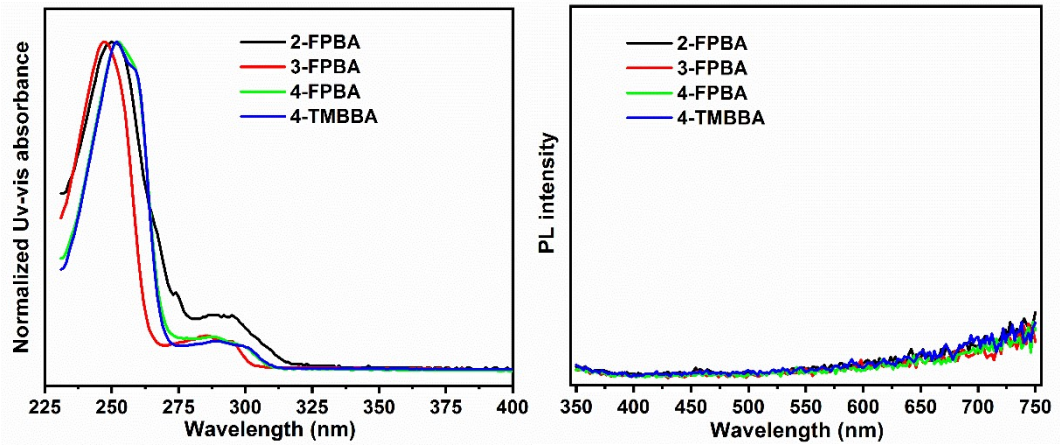

Figure S4. The absorption (left) and emission (right) spectra in 2-methyltetrahydrofuran solution at room temperature.

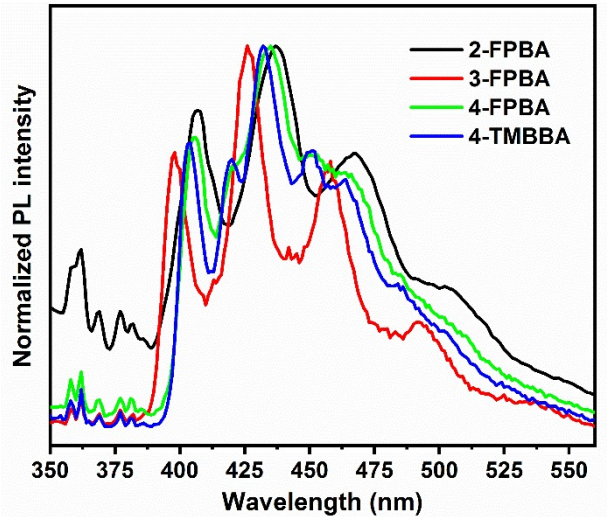

Figure S5. The emission spectra in 2-methyltetrahydrofuran solution at 77 K.

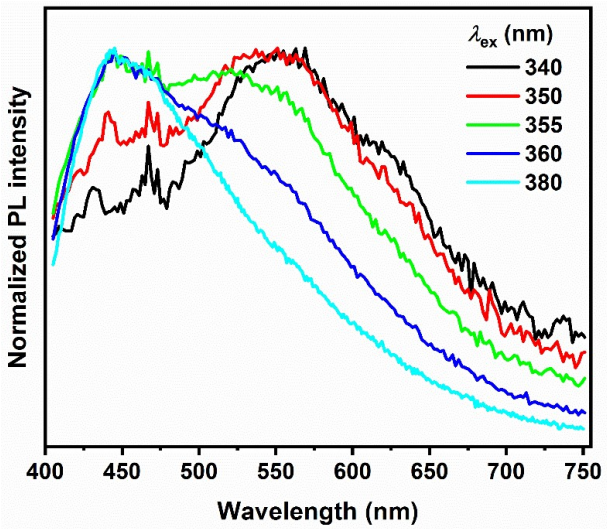

Figure S6. The normalized emission spectra of 2-FPBA at different excitation wavelength.

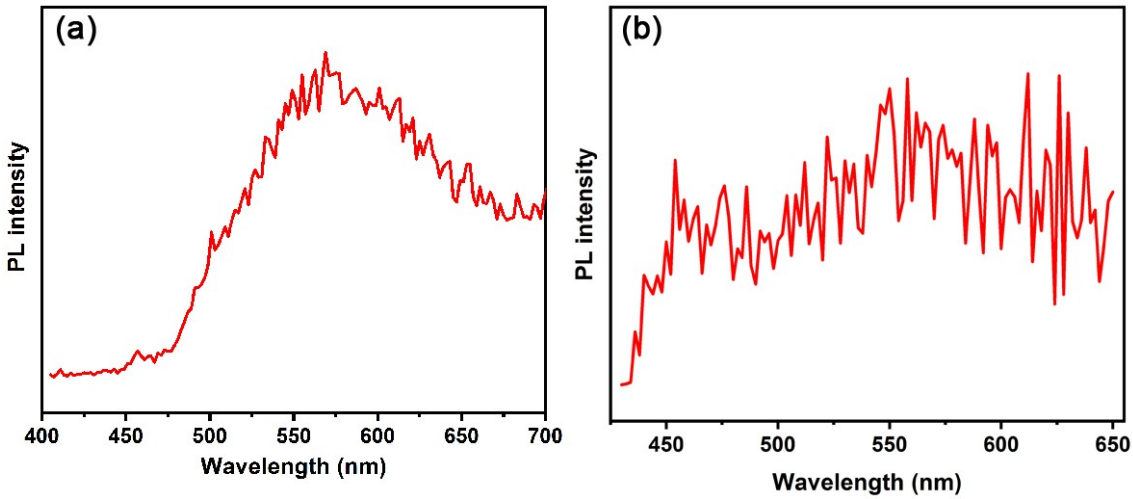

Figure S7. (a) The 100 us-delayed emission spectra of 2-FPBA solid at room temperature (λ_{ex} = 355 nm). (b) The 50 us-delayed emission spectra of 3-FPBA (λ_{ex} = 395 nm).

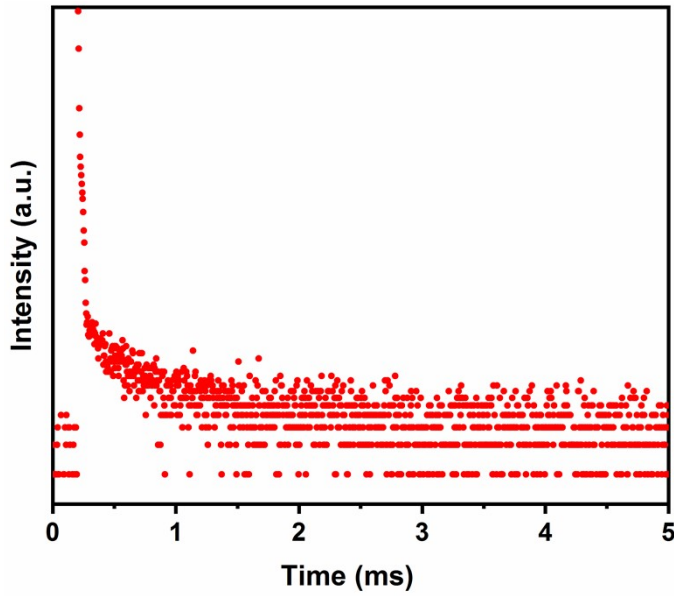

Figure S8. The phosphorescence decay curve of 3-FPBA monitor at 565 nm (λ_{ex} = 380 nm).

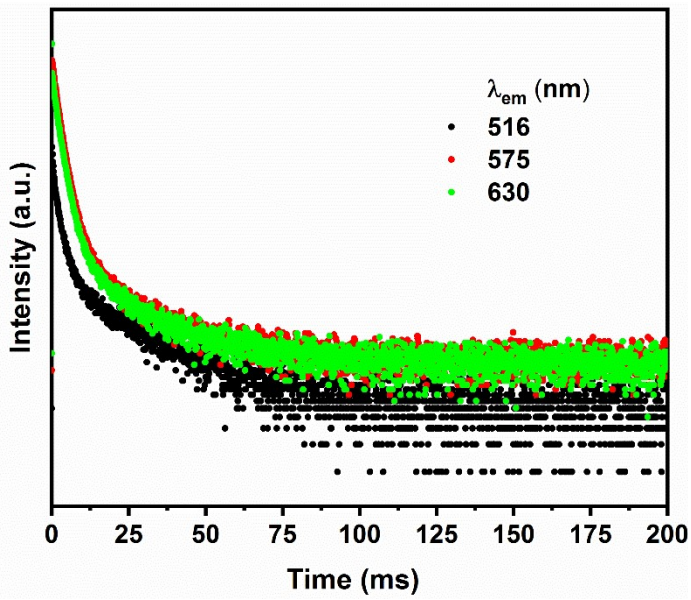

Figure S9. The phosphorescence decay curves of 4-FPBA monitored at different emission wavelength.

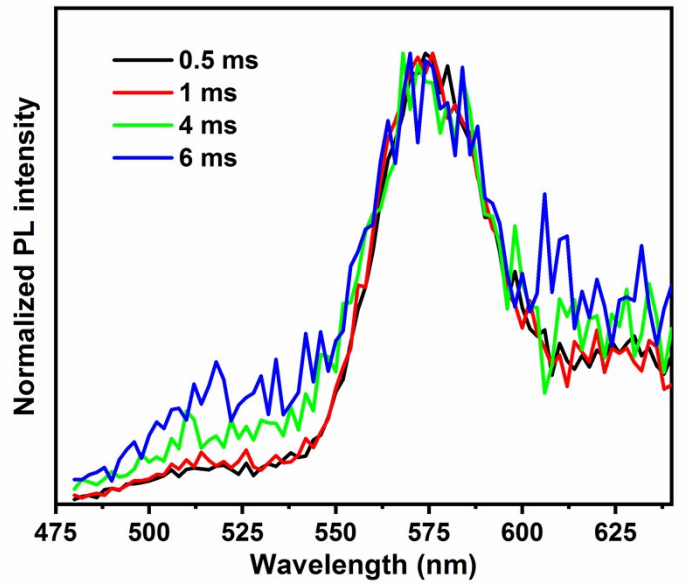

Figure S10. The RTP spectral change of 4-FPBA with delay time.

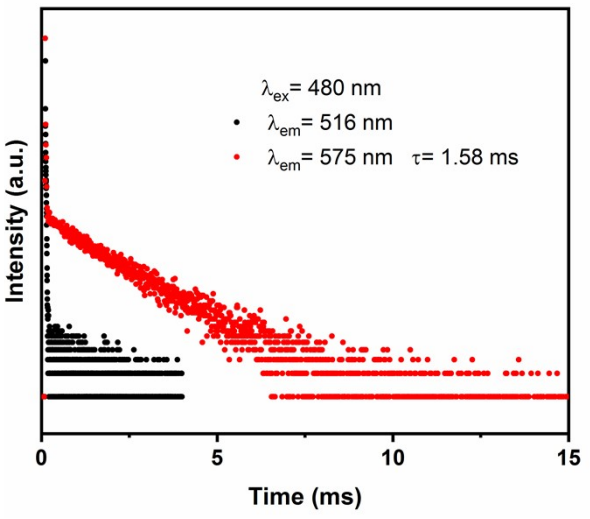

Figure S11. The phosphorescence decay curves of 4-FPBA under 480 nm excitation.

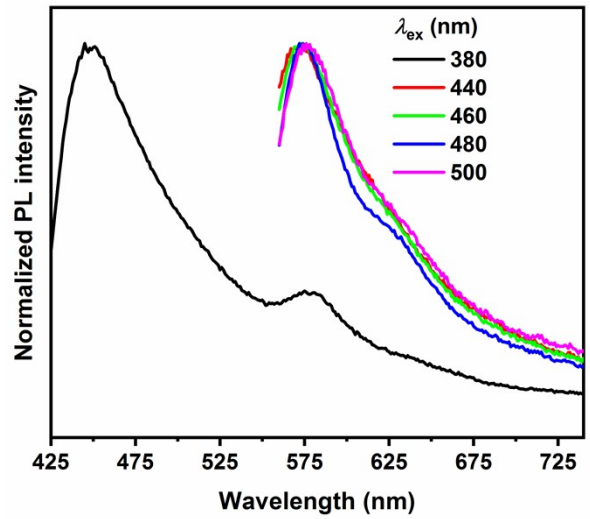

Figure S12. The emission spectra of 4-FPBA under low-energy excitation.

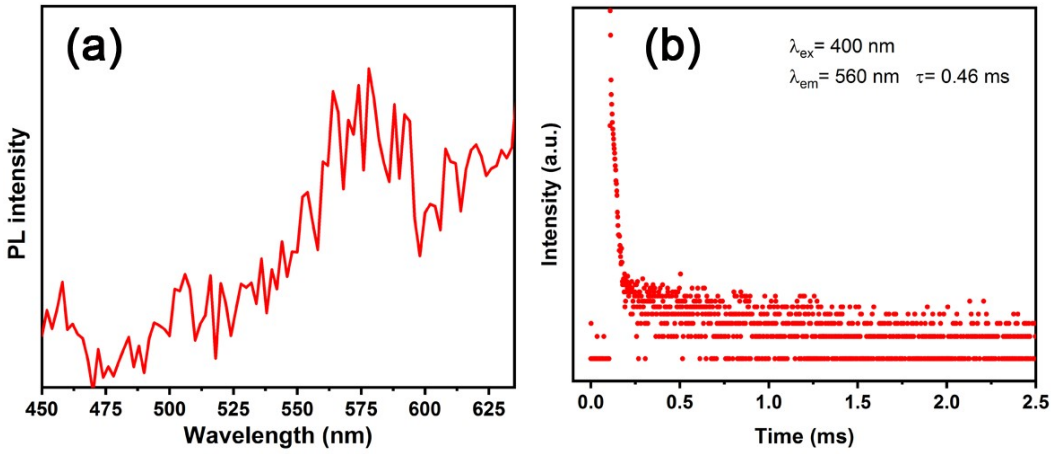

Figure S13. (a) The 50 us-delayed emission spectra of 4-TMBBA solid at room temperature (λ_{ex} = 400 nm). (b) The phosphorescence decay curves of 4-TMBBA monitored at 560 nm.

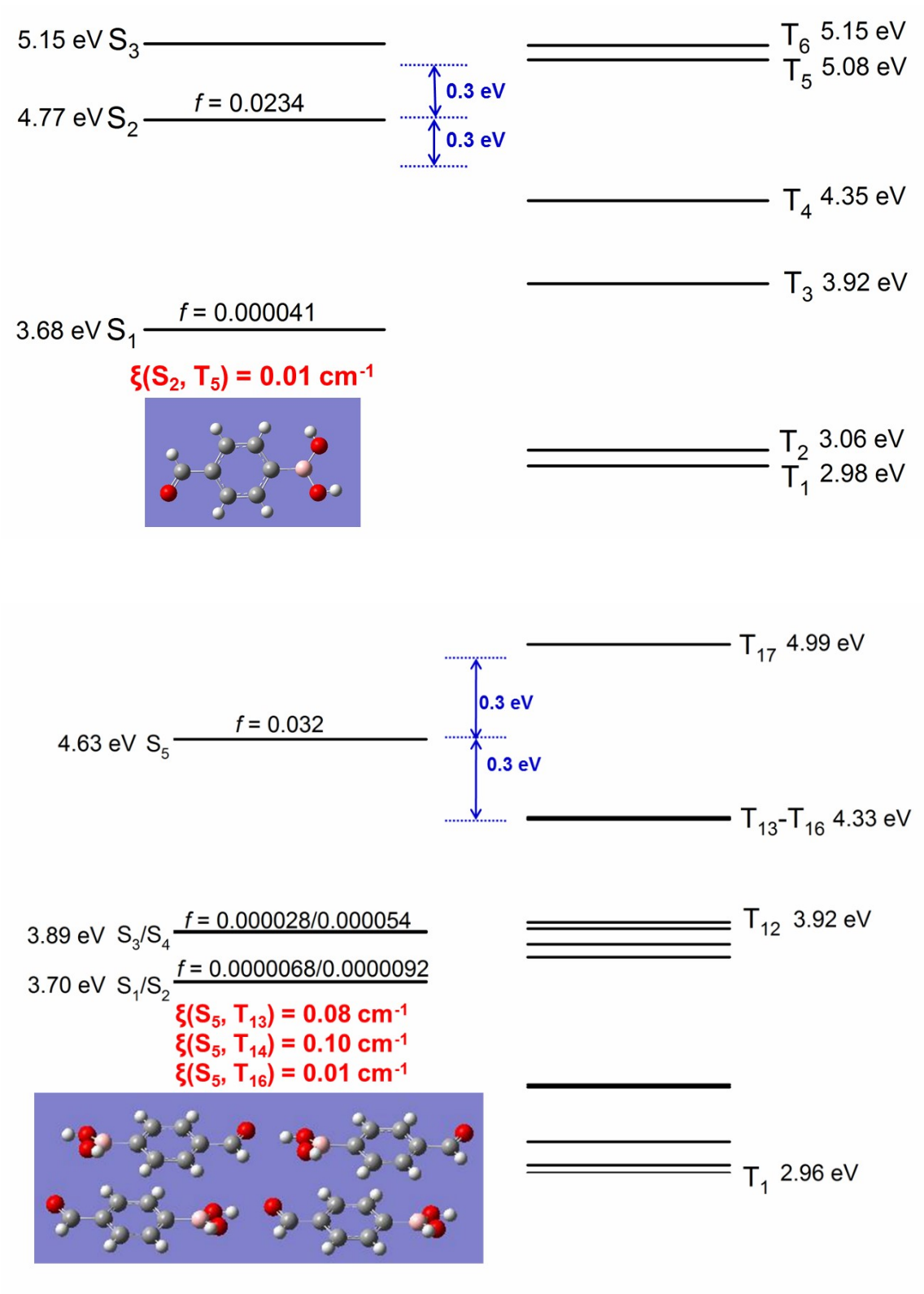

Figure S14. The calculated energy level of 4-FPBA single molecule (top) and tetramer (bottom) and the SOC values (ξ) between interested S and T. The molecule geometry was directly obtained from the crystal structure.

Table S2. X-ray crystal structural data.

	2-FPBA	3-FPBA
Chemical formula	$C_7H_7BO_3$	$C_7H_7BO_3$
Formula Mass	149.94	149.94
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	3.889(2)	22.750(7)
b/Å	13.249(8)	3.8166(11)
c/Å	14.043(9)	17.211(5)
α/°	90	90
β/°	91.986(9)	101.691(4)
γ/°	90	90
V/Å^3	723.1(8)	1463.4(7)
Temperature/K	296(2)	296(2)
Z	4	8
Density/Mg/m^3	1.377	1.361
No. of reflections measured	1591	1499
No. of independent reflections	1591	1499
R_1 (I> 2σ(I))	0.0562	0.0439
wR_2 (I> 2σ(I))	0.1779	0.1252
R_1 (all data)	0.0685	0.0585
wR_2 (all data)	0.1929	0.1377
Goodness of fit on F^2	1.154	1.009

References

[1] G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112-122.

[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341.

[3] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.*, **2020**, *152*, 224108.

[4] P. R. Spackman, M. J. Turner, J. J.McKinnon, S. K. Wolff, D. J. Grimwood, D. Jayatilaka, M. A. Spackman, *J. Appl. Cryst.*, **2021**, *54*, 1006-1011.